

## Optical pH Sensor Based on Quinizarin for Alkaline pH Regions

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### ABSTRACT

**T**he development of an optical pH sensor based on immobilization of quinizarin (1,4-dihydroxyanthraquinone) on a triacetylcellulose membrane was described. The resulting membrane exhibited fast color change from yellow to violet, while changing the pH in alkaline region. The immobilized quinizarin showed a broader dynamic range from (pH 9.4-11.4) with respect to free form (pH 8.8-10.4). The sensor response was fully reversible and fast (<20 s) under the batch conditions with pH between 7 and 12.5. The sensor showed excellent long term stability (more than three months) and high reproducibility (R.S.D. less than 2%). The  $K_a$  values for free and immobilized dye were evaluated and the chemical reactivity of the quinizarin in solution and after immobilization was also described. Prog. Color Colorants Coat. 1(2008) 11-17. © Institute for Colorants, Paint and Coatings.

## 1. Introduction

The developments of optical sensors have recently grown rapidly because of their possible applications in biotechnology, ecology and medicine [1, 2]. Researchers are also interested in such sensors with respect to cost, freedom from electrical interference, safety, possibility of remote sensing and real time analysis. In recent years, several photometric and optometric sensors for the selective determination of cationic and anionic species have been reported in the literature [3-8].

Optical pH sensors have attracted the most attentions because of the importance of pH measurement in various scientific researches and practical applications [9]. These sensors are based on pH-dependent changes of the absorbance or luminescence of certain indicator molecules

being immobilized on/in solid substrates [10]. There are different reports on optical pH sensors, but for alkali range they are rare [11].

Anthraquinones are extremely important when we are taking into account their properties and broad field of their applications [12]. For years their chromophoric system has been used extensively to prepare the textile dyes [13]. They are also compounds of significant chemical and biochemical interest. These molecules have important applications as a prominent family of pharmaceutical active and biological relevant chromophores and an analytical tool in determination of metals [14, 15].

In this work, the construction of an optical pH sensor based on immobilization of quinizarin (1,4-dihydroxy-

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anthraquinone) on an optically transparent triacetyl-cellulose has been described. The optical and chemical properties of the sensor as a function of pH are evaluated by spectroscopy. The  $K_a$  values for free and immobilized dye have been evaluated and chemical reactivity of quinizarin in solution and after immobilization has been also described.

## 2. Experimental

### 2.1. Reagents

Quinizarin (1,4-dihydroxyanthraquinone) was supplied by Merck. All other reagents were analytical reagent grade. The indicator was immobilized on a transparent triacetyl-cellulose film, produced from waste photographic tapes. pH buffer solutions were prepared as discussed by Bates [16].

### 2.2. Instrumentation

All spectrophotometric measurements were recorded by using a Shimadzu Multi spec-1501 Photo Diode Array Spectrophotometer. A Metrohm 713 pH-meter calibrated with Merck pH standards and a double junction glass electrode was used for pH adjustment.

### 2.3. Membrane preparation

The transparent triacetylcellulose membranes were produced from waste photographic film tapes. Films previously treated with commercial sodium hypochlorite in order to remove colored gelatinous layers for 12 hrs at room temperature. De-estrification of the acetyl groups and increasing the porosity of membranes were done by treating in 0.1 M NaOH for 2 hrs at room temperature as described previously [17-19]. Then, the films rinsed 3 times with cold water until being neutralized and kept in distilled water for 12 hrs. For immobilizing of quinizarin on the films, a 0.01% quinizarin solution was used in which the films were dipped in for 10 mins. at room temperature under stirring. After immobilization of quinizarin, the films ( $8 \times 30 \text{ mm}^2$ ) were put inside the commercial quartz cell ( $1 \times 1 \times 4.4 \text{ cm}^3$ ) containing the test solution and the acid-based behavior of the films were studied by the spectrophotometric measurements of the samples at maximum wavelengths of basic forms of free and immobilized quinizarin (540 nm and 550 nm respectively) in buffered solutions.

## 3. Results and discussion

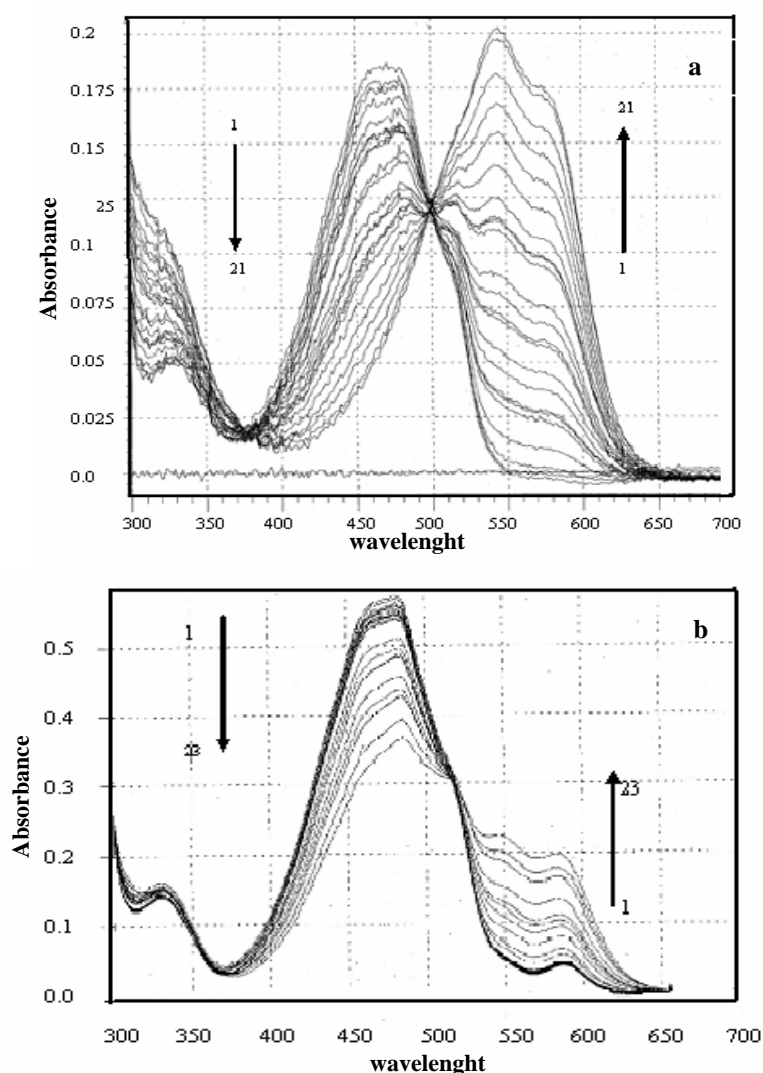
The optical properties of quinizarin in solution and immobilized on a hydrolyzed cellulose acetate films, are shown as a function of pH in Figure 1. Spectral changes are the results of acid-based equilibriums. These changes are completely reversible with the variation in pH. The spectra show that quinizarin in solution and the immobilized form has exhibited very different characteristics in optical and acid-based behavior. It is clearly obvious that the absorption spectra of the immobilized form is red shifted, with respect to its soluble form, having absorption maxima at 485, 550 and 585 nm at the two extrem values (in comparison with the solution having maxima at 470, 540 and 575 nm).

Dissociation constants were evaluated from the computer fitting of the absorbance-pH data (Figure 2) to equations that resulted from substituting the pH and absorbance values in the mass balances [20-21]. The resulting equation for diprotic acid is given as:

$$A = \frac{A_0 + (A_1[H^+]/K_2) + A_2([H^+]^2/K_1K_2)}{([1 + [H^+]/K_2] + ([H^+]^2/K_1K_2))} \quad (1)$$

Where  $A$  is the observed absorbance at each titration point,  $A_0$ ,  $A_1$  and  $A_2$  are the absorbances of the basic form, monoprotonated form and diprotonated form, respectively, and  $K_1$  and  $K_2$  are the first and second acidity constants. The  $A_0$ ,  $A_1$ ,  $A_2$ ,  $K_1$  and  $K_2$  values were calculated by computer fitting of the absorbance-pH data to eq.1 by using a nonlinear least-squares program, written on the basis of the Gauss-Newton algorithm [21]. Calculated values for  $pK_{a1}$  and  $pK_{a2}$  are  $9.8 \pm 0.01$  and  $12.56 \pm 0.02$  for free and  $10.96 \pm 0.01$  and  $14.38 \pm 0.02$  for immobilized forms of quinizarin, respectively. Calculated  $pK_{a1}$  and  $pK_{a2}$  in solution shows good agreement with previous reported values [22].

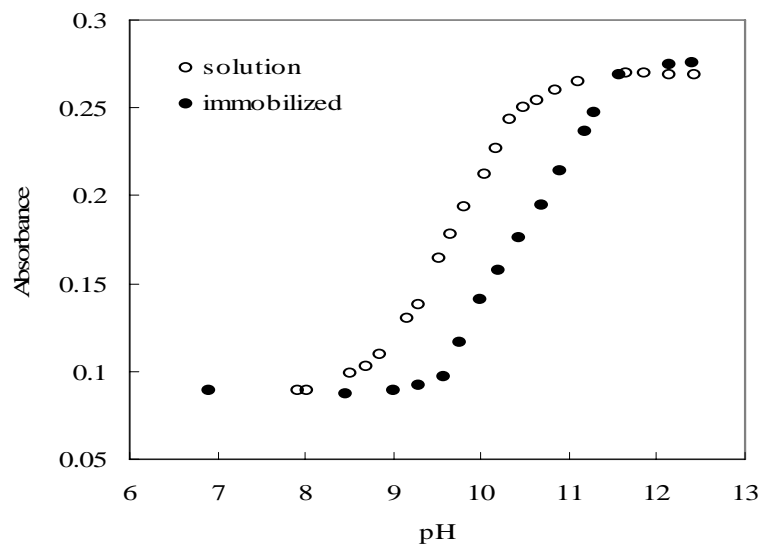
The above results can be interpreted on the bases of the influence of quinizarin immobilization.  $pK_a$  values, are also affected by the micro-environment interactions of quinizarin with the medium. Similar observations were reported by others [14, 15, 17, 23]. The fact that quinizarin immobilization changes the absorption maxima, shows that hydroxyl groups are auxochrom elements of molecule and also, shows a proton loss, influences charge distribution during the dissociation of the dye immobilized.



**Figure 1:** Absorption spectra of quinizarin in: **a)** free (0.001% quinizarine) pH: (1) 7.93, (2) 8.03, (3) 8.52, (4) 8.70, (5) 8.86, (6) 9.17, (7) 9.81, (8) 9.30, (9) 9.53, (10) 9.66, (11) 10.05, (12) 10.18, (13) 10.32, (14) 10.49, (15) 10.64, (16) 10.86, (17) 11.10, (18) 11.66, (19) 11.85, (20) 12.15, (21) 12.43. **b)** immobilized form (0.0001 mol l<sup>-1</sup> quinizarine) pH: (1) 6.90, (2) 8.47, (3) 9.57, (4) 10.06, (5) 10.19, (6) 10.30, (7) 10.38, (8) 10.43, (9) 10.59, (10) 10.72, (11) 10.99, (12) 11.11(13) 11.15, (14) 11.26, (15) 11.41, (16) 11.55, (17) 11.60, (18) 11.75, (19) 11.85, (20) 11.95 (21) 12.14, (22) 12.24, (23) 12.36. Arrows indicate the spectral trends in changing pH from 7.93 to 12.43 in a) and 6.90 to 12.36 in b).

The calibration curve and the dynamic response range of quinizarin in free and immobilized form are shown in Figure 2. These curves show that immobilized quinizarin has 0.5 pK<sub>a</sub> units (pH = 9.4 and 11.4) wider than free form (pH = 8.7 and 10.5) in dynamic working range. It has been suggested that the wider dynamic range is due to multiple different interactions between the immobilized indicator and the substrate. The same

behavior was also reported previously [12, 23-25]. Changes in absorption maxima, pK<sub>a</sub> and dynamic range before and after dye immobilization show that the dye in the membrane matrix exists in two forms; the absorbed and free form. The adsorbed form is responsible for the extended pH range. This indicates that a weak physical interaction between the quinizarine and acetate groups of cellulose exists.



**Figure 2:** Response curve as a function of pH for quinizarin in ○) solution (0.001 wt% quinizarine) (540nm) and ●) immobilized form ( $0.0 \cdot 01 \text{ mol}^{-1}$  quinizarine) (550 nm).

Reproducibility, reversibility and the response time are the important characteristics of a sensor. The response time is defined as the time required for 95% of the total signal change [12] (Figure 3). It shows a typical response for the transition process as a result of change in pH solution in contact with the optode from pH of 9 to five successive pH values of 9.5, 10, 10.5, 11 and 11.5 at 550 nm. It should be noted that the signals leveled off after equilibrium and no drift in the response time was observed. As it can be seen the response time of the sensor was measured as 20 second (Figure 3). Also, the repeatability of the quinizarin sensor was evaluated by repeating the variation of pH. The relative standard deviation for the change in the membrane response was obtained about 2%.

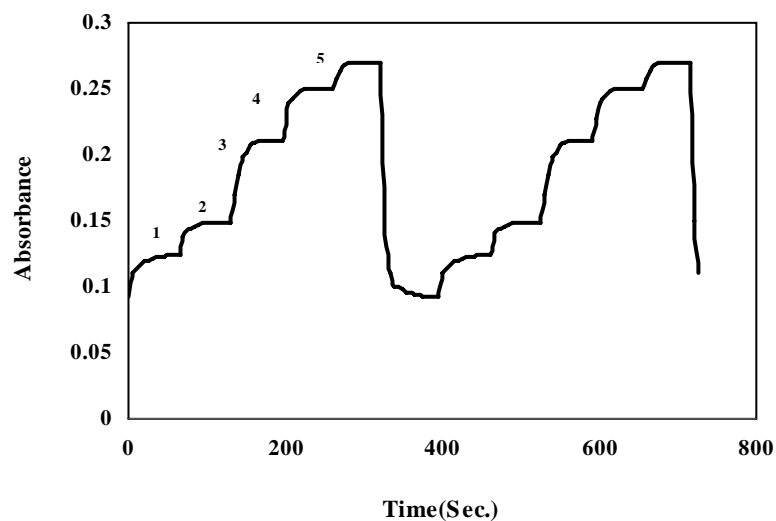
In order to investigate on the short term stability of sensor, the sensor response was monitored for a period of 6 hrs in pH of 10. Results showed that it was stable over the pH applied with no leaching of the dyes. It was found that the optode is also stable over the successive pH measurements in the pH range of 8-12 for 6 hrs. In order to investigate the long term stability of the sensor, the sensor response was measured over a period of 100 days. As it can be seen in Figure 4 the response is almost complete with only 8 % decrease in the absorbance. High sensitivity in the alkaline region, fast response times and good reversibility membranes are desired in constructing

suitable sensors for measuring high pH values.

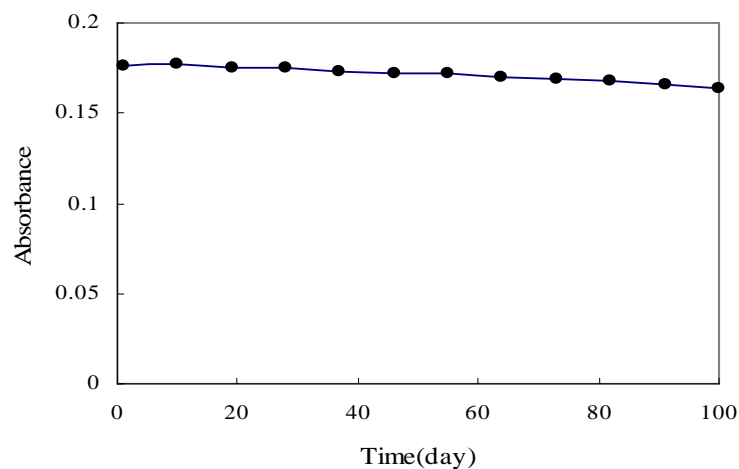
One limiting factor for optical pH sensors in real sample analysis, is the effect of ionic strength on the dissociation constant of indicators that would cause a pH error measurement. The influence of ionic strength on the absorbance response of the sensor using solutions with 0.0, 0.1 and 0.2 M NaCl is shown in Figure 5. The  $pK_a$  value of quinizarin decreases in the order of 11.15, 10.93 and 10.55 with the increasing ionic strength of the sodium chloride solutions in the order of 0, 0.1 and 0.2 M, respectively. It has been found that, in pH optical sensors with increasing ionic strength, the acidity of quinizarin increases [13-15, 23].

Thus the ionic strength of the system under analysis should be recorded and should remain constant during pH measurement procedures. In this work, all of the experiments were done at ionic strength of 0.1 M of NaCl.

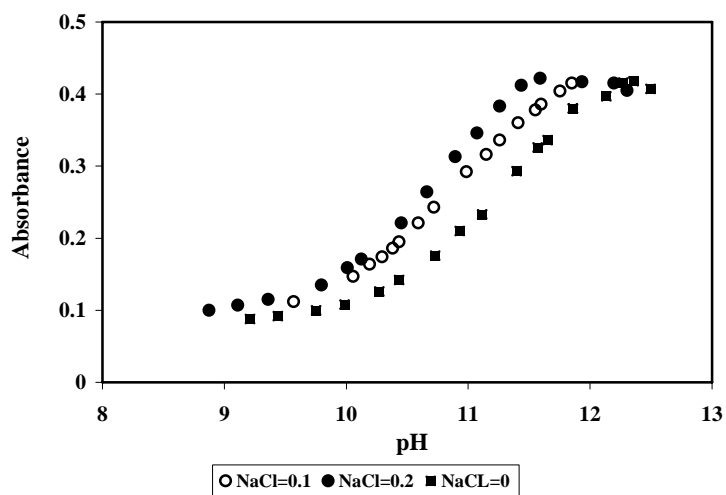
Quinizarin is an indicator for spectrophotometric measurement of lithium and magnesium ions. It shows high selectivity, since the 'O'-donors are blocked by two strong intramolecular hydrogen bondings. The interference of metal ion complexation with the optical response of the sensor has been examined using lithium as a test ion. In solution, quinizarin selectively forms complex with  $\text{Li}^+$  ions at alkaline pH region [4].



**Figure 3:** Absorption as a function of time for quinizarin sensor in the transition process from pH of 9 to 5 successive pH values of 9.5, 10, 10.5, 11 and 11.5 (550 nm).



**Figure 4:** Absorbance - time plot of quinizarin sensor at 550 nm (long term stability) pH 10.



**Figure 5.** Calibration plots of quinizarin sensor at ionic strengths of 0, 0.1 and 0.2 M of NaCl .

**Table 1:** Response characterizations of some pH optical sensors.

Sensor base	Chromophore	Response time	pH range	Reference
Triacetylcellulose	Victoria bue, Dipycrylamine	45 s	0-3 ,10-13	11
Diacetylcellulose	Phenolphthaleine	2-30s	8-12.5	12
Triacetylcellulose	Thiazole yellow	27s	12-13.5	17
Triacetylcellulose	Dipycrylamine	-	0-3.2	22
Conductive polymers	Polyaniline	1s	5-7	23
Triacetylcellulose	quinizarine	10s	9.4-11.4	This work

However, when it is covalently immobilized at a triaceylcellulose film, the absorption spectra, with and without  $\text{Li}^+$  ion have been the same for 10 mins. This indicates that the complexation of Q with  $\text{Li}^+$  ion interfere within the response of the sensor. It seems that the diffusion rate of lithium ion from bulk into the membrane is much slower than hydrogen ion which is related to their mobility and ionic radii, and the characterization of the membrane and the solution matrix. The sensor responses no change in the presences of other alkaline and alkaline earth metal ions. Furthermore, most of transition metal ions precipitate in the working pH range of the sensor. Thus, it seems likely that the sensor will be free from complexation existing in lithium and other metal ion interferences.

#### 4. Conclusions

A waste cellulose acetate film with good optical and mechanical properties is used as a matrix for quinizarin immobilization. The above results show that the

application of quinizarin immobilized on acetylcellulose membranes can offer a suitable sensor for pH measurement in the alkaline region of pH scale with wide dynamic range. The response of the sensor is reproducible with the longer linear dynamic range in relation to free quinizarin form. The films have shown fully reversible color change in the pH range from 7-12.5. Results have indicated that the optode can perform fast response and continuous use for at least three months. The sensor has showed good characteristics among other optical pH sensors reported so far. (Table 1).

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